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TUNG HULLS AND PRESS CAKE

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Burning tung hulls at a hulling plant

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Agricultural Research Administration

Bureau of Agricultural and Industrial Chemistry

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Photograph on cover shows the burning of tung hulls at a hulling plant.

TUNG HULLS AND PRESS CAKE

by

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INTRODUCTION

Tung oil, one of the most prized of the drying oils, is produced from the fruit of the tung tree (Aleurites fordii), a member of the Euphorbia family native to China. The fruit is about 2 inches in diameter and normally has 4 or 5 seeds (See Fig. 1). The entire fruit is covered by a spongy outer hull about a quarter of an inch thick. Each kernel is coated by a hard shell, and the seed is enclosed by a thin papery inner hull. The kernels contain about 65% oil and constitute about a third of the weight of the fruit.

From time immemorial, China has been the world's chief supplier of tung oil. Before World War II the United States imported as much as 175,000,000 pounds annually from China. The supply was cut off during World War II.

The first tung trees were introduced into the United States in 1905, but sizeable plantings were not made until about 1924. The first tank car of tung oil was shipped from Gainesville, Fla., in 1932. The acreage has expanded to about 200,000 acres in 1952, with an estimated production of 120,000 tons of fruit from the 1952 crop.

In the United States the oil is obtained usually by pressing the ground hulled fruit in continuous screw presses. Before being pressed the fruit is hulled in disc hullers, and the hulled fruit is dried if necessary to about 10 percent moisture content. It is then ground in an attrition mill and put through the steam jacketed screw presses. The oil is extruded through spaces between bars comprising the barrel of the press, and the cake, containing 3.5 - 6.0% oil, is extruded at the end of the press. The crude oil when filtered through a plate-and-frame filter press is ready for the market.

Tung hulls and press cake are the byproducts of the production of tung oil. More profitable uses for these byproducts would help place the tung industry on a sounder economic basis. The purpose of this report is to consider the utilization of these materials on the basis of their composition and amounts available.

Practically all the outer and inner hulls and a varying proportion of the shell are removed in the hulling operation. In this report the term "hulls" is used to denote commercial hulls which consist of a mixture of the outer hulls, inner hulls, and shell. When the hull components are mentioned separately, they are referred to as inner hull, outer hull, or shell.

Tung fruit is hulled either at the tung mills or at the orchard. The large piles resulting from hulling at the orchard are either allowed to remain where they fall or are spread in the orchard. If a better market is not developed for tung hulls, more and more of the hulling will probably be done in the orchards to save the expense of hauling the additional weight to the mill.

The dry fruit is composed by weight of about 39% outer hull, 7% inner hull, 21% shell, and 33% kernels. Since a part of the shell usually remains with the kernels in the hulled fruit, the weight of hulls obtained in commercial hulling is about 60% of the weight of the fruit. The production of tung fruit for 1952 is estimated to be 120,000 tons and on this basis there will be about 72,000 tons of tung hulls for disposal. These hulls will be distributed in location approximately as follows: eastern Louisiana, 20,600 tons; southern Mississippi, 35,700 tons; southern Alabama, Georgia and northern Florida, 15,700 tons.

A limited amount of hulls is ground and sold to fertilizer companies for use as a conditioner in mixed fertilizers. Some of the hulls are also hauled back to the grove and spread over the soil as a source of organic matter or used to mulch ornamentals, but in the main, the hulls constitute a nuisance and most of them are burned.

Review of Literature

Phillips found (12) that tung shell contained 44.8% lignin, 12.1% alcohol-benzene extract, and 9.8% furfural. He also determined ash, methoxyl, hot-water extractives, 1% hydrochloric acid extractives, and uronic acids, and obtained a vanillin yield of 3.2% based on the weight of the shells which was equal to a yield of 6.4% based on the weight of lignin.

Sell, Johnsonton, and Lagasse (14) collected samples of tung fruit at intervals from the last of June to the last of November, and separated the fresh fruit into hull, outer integument, shell, and kernels. They analyzed these components for nitrogen, reducing sugars, non-reducing sugars, starch, and polysaccharides. In mature fruit, the sample taken November 29, they

found the hull to contain 0.47% nitrogen, traces of reducing and non-reducing sugars, 1.2% starch, and 9.4% polysaccharides. The outer integument contained 1.11% nitrogen, traces of reducing and non-reducing sugars, 1.2% starch, and 4.3% polysaccharides. The shell contained 0.44% nitrogen, traces of reducing and non-reducing sugars, 0.38% starch, and 9.2% polysaccharides.

In 1941-3, the Eastern Regional Research Laboratory of this Bureau analyzed a number of samples of tung hulls (outer and inner hulls) for tannin (17). The usual method for tannin-determination showed 4-7% tannin in fresh hulls, but this substance had no value for tanning leather. It would not penetrate the leather, but formed a very hard coating on the surface. One sample of weathered hulls showed less than 1.0% tannin.

In 1945, a sample of tung hulls (outer and inner) was analyzed at the Western Regional Research Laboratory by the Biochemical Division for ascorbic acid (17). The sample was found to contain only 0.03% ascorbic acid, a value too low to offer possibilities as a commercial source of this acid. Similar determinations of ascorbic acid made by the University of Florida on similar samples of hulls showed ascorbic acid contents as high as 0.68%.

Experimental

Preparation. Commercial hulls vary in proportions of outer and inner hulls and shell, and are of unknown history with respect to conditions of hulling, length of weathering or storage, etc. To obtain a sample of known proportions and history, a batch of freshly fallen green tung fruit was picked up, rinsed off quickly in water to get rid of adhering dirt, and air-dried. The fruit was then riffled into eight subsamples. The outer hulls, inner hulls, and shell were separated from these samples by hand, and analyzed separately, because differences in physical appearance indicated the possibility of differences in chemical composition. The composition of the total hull sample was calculated from the weights and analyses of the three components.

Since the outer hull is high in water-soluble substances, and the tung belt is an area of high rainfall, the composition of weathered hulls would differ from that of the fresh hull, depending upon the amount of leaching the fruit has been subjected to before harvest.

One of the eight subsamples was separated and analyzed immediately. The other 7 were exposed to the weather by spreading them on burlap bags on the ground, and were separated and analyzed at intevals throughout a total weathering period of 6 months.

Methods of analysis. Hull components were analyzed for pentosans, lignin, cellulose, a-cellulose, hot-water solubles and alcohol extractables by methods of the Forest Products Laboratory (8), in the last case alcohol being substituted for the alcohol-benzene mixture specified by the method; and for nitrogen and potash (2a, b) by official methods of the Association of Official Agricultural Chemists, except that the method for nitrogen was modified by using boric acid for the absorption of ammonia. Ash was determined by incineration in an electric muffle for 4 hours at 650° C., and phosphoric acid by the method of Gerritz (9) modified by the use of sulfuric acid and hydrogen peroxide for digestion of the samples. Copper, iron, and manganese were determined spectroscopically.

Results and Discussion. The composition of fresh hulls and hulls weathered for 2 and 6 months is given in Tables I and II.

The fresh hulls are composed mostly of lignin, cellulose, and pentosans. The inner hulls are highest in cellulose (46%) and pentosans (18%), and the shell highest in lignin (51%). The cellulose content of the inner hulls (46%) is equal to that of many other agricultural residues, but the cellulose contents of the outer hull and shell are low compared with cellulose in most residues (11). The outer hull has a high content of hot-water solubles (39%) and the shell has a high content of alcohol solubles (17%). The potash content (2.4% on total hulls) is high enough to give the hulls some value as a soil fertilizer.

The most striking changes in composition on weathering are the decreases in percentages of water-solubles and increase in percentage of lignin in the outer hulls. It was calculated from these analyses and the corresponding weights of the components that after 6 months of weathering, the water soluble components in the total hull sample had decreased by three-fourths, the potash by one-half, the cellulose and pentosans by one-fifth, while the amount of lignin had not appreciably changed.

Utilization of Tung Hulls

In considering the utilization of a low value product like tung hulls one of the important factors is the cost of handling and transportation. Freight on tung hulls in car load lots from Bogalusa, La., to Jackson, Miss., a distance of about 110 miles, is $4.80 per ton. On this basis the cost of shipping is nearly as large as the price of the hulls at the mill, $6.00 to $7.00 per ton during the 1951-52 season.

Fertilizer Conditioner. Ground tung hulls are used to a limited extent as a conditioner in mixed fertilizers. A greater volume of this material probably would be used, if it were not for the danger of spontaneous heating and ignition in stored ground hulls. Fertilizer companies hesitate to store the material in view of this characteristic.

It is probable that tung hulls of high moisture content heat spontaneously as do many other agricultural products. Unpublished work of this laboratory has indicated that hulls containing more than 17% moisture heated spontaneously while hulls containing 15% or lower moisture did not display this difficulty. This problem may be overcome by drying the hulls and then grinding them, but the value of the hulls may be so low ($6.00 - $7.00 per ton at the mill) that it may not be economically feasible to dry them.

Mulching Material. There is some demand near tung mills for tung hulls as a mulching material for ornamental shrubs. However, fresh hulls should not be used in too great an amount as shrubs and even tung trees have been injured or killed from use of too many fresh hulls, presumably from the heavy application of potash or other unidentified constituent(s) of the hulls. Partly rotted hulls would make a better and safer mulch.

Adding Organic Matter to Soils. At many mills the hulls are available to the growers without charge. These hulls would have some value as a source of organic matter and potash and could be spread profitably in tung groves or on other land. However, the hulls are available when growers are busy with harvesting and when the groves are often too wet to drive trucks into them. Hence, growers are reluctant to return the hulls to their groves.

Compost. While hulls have not been used to any appreciable extent for making composts, no doubt good composts (16) could be made by piling the hulls, incorporating mineral fertilizers and keeping the pile damp. The problem would be in developing a market. The handling of a compost is too expensive for general farm practice and would be justified only in growing high-priced specialty crops.

Fuel. Tung hulls are burned as a fuel under boilers in at least one mill. These boilers have specially constructed grates for burning hulls. The calorific value of tung hulls is about 7160 B.T.U. per pound for hulls containing 12.3% moisture, which corresponds to 8300 B.T.U. for dry hulls, a value slightly less than for wood. When hulls are used as a fuel, auxiliary fuel must be available on starting up the mill, unless hulls are stored from the previous season for this purpose. Also, at times the hulls may be too wet to burn, and for such an eventuality provision must be made for drying them.

Potash. Several years ago one of the mills burned all its hulls, and sold the ash as a source of potash. With potash priced at $36.25 per ton of 92.5% potassium sulfate, the potash in a ton of hulls containing 2.45% K_2O would be valued at $1.78.

Plastics. There would seem to be little likelihood of using tung hulls in plastics, because they have a high content of water solubles and because they would have to compete with pressed woods, corncobs, bagasse, etc., materials that are available in far greater quantities than are tung hulls. In many plastics, the cost of raw material is a minor part of the total cost of the finished articles which is due largely to the cost of manufacture and distribution.

Chemicals. As a possible source of chemicals, the nature of the alcohol extractables in the shells, and of the water extractables in the outer hulls should be determined. The shell contains about 15% of material extractable by alcohol. The fresh outer hull contains about one-third water soluble substances. This is neither sugar nor tannin. Its nature should be studied further.

Tannins. Tannin-extract from pecan hulls has been used in oil-well drilling muds to control viscosity of the mud. Purified forms of lignin have also been used for the same purpose. The water-extractables of tung hulls should be tested, to determine if this method has any possible use in drilling muds.

A 7% tannin content in 72,000 tons of hulls would amount to 10,000,000 pounds of 100% tannin, which is very small compared to the average of 250,000,000 used in the United States annually (15).

TUNG PRESS CAKE

An average of about 350 pounds of press cake is obtained from each ton of tung fruit. With an estimated tonnage of 120,000 tons of fruit for the 1952 crop, there will be about 21,000 tons of press cake available. This press cake would be located about as follows: 6000 tons in Louisiana, 10,400 tons in southern Mississippi, and 4,600 tons in northern Florida and adjacent areas of southern Alabama and Georgia.

Only a few data have ever been published on the composition of press cake (4, 13). To determine the range in composition of press cake, samples were collected from domestic mills and analyzed.

Experimental

Preparation. Twenty-five samples, including one or more from each of the 14 mills operating in the tung belt of the southeastern United States, were collected. Gallon samples were obtained as the cake issued from the press. The samples were ground in a cutting mill through a 1-mm. screen.

Methods of Analysis. The ground samples were analyzed for pentosans, nitrogen, ash, phosphoric acid, potash, copper, iron, and manganese by the same methods used for hulls. These samples were also analyzed for oil (1) and for crude fiber (2c) contents.

Results and Discussion. The results of analyses are given in Table III. The nitrogen content on a moisture-free basis, averaging 3.9%, ranged from 3.0% to 4.9%. On the undried samples this average would correspond to about 3.7% nitrogen or 23.1% protein.

The sale of tung press cake as fertilizer has usually been based on a 4% nitrogen content. Probably in the first years of the domestic tung oil industry the nitrogen content of the press cake averaged 4.0%, or higher. However, as more mills installed driers they were able to hull wetter fruit, and to dry the hulled seeds before processing. The present lower nitrogen content of press cake can probably be explained by the fact that more hull and shell are left with the hulled material delivered to the presses.

Utilization of Tung Press Cake

Fertilizer. All tung cake has been sold as fertilizer. In common with other oilseed meals, tung cake is a good source of organic nitrogen. The nitrogen of oilseed cakes and meals is not water soluble until the cake is decomposed by soil micro-organisms. Thus the nitrogen of tung press cake becomes gradually available over a period of several months as the cake is broken down by soil micro-organisms, making it a very good nitrogen fertilizer for the sandy soils of the tung belt.

Stock Feed. The high protein content of tung press cake would indicate that it might be of value as a stock feed, but unfortunately it contains a substance or substances which are toxic to animals. Considerable work has been done on the toxicity of press cake. Rusoff, Mehrhof, and McKinney (13) fed solvent extracted press cake, which had been freed of solvent by steaming at 330°F. and stored for a considerable length of time, to 12-day old chicks. They observed no definite signs of toxicity when the meal amounted to as much as 20% of the rations, although the chicks on rations including the cake consumed less and gained less in weight. Erickson

and Brown (7) found oil-free tung kernels to be highly toxic to rats, but the oil to be non-toxic. The meal could be detoxified by heating with steam for 2 hours at 230°F. Alcohol extraction removed the toxic character of the meal, but the toxic principle(s) could not be recovered from the alcohol extract.

Emmel (5,6) identified saponin as a toxic principle in tung leaves and kernels. The toxic character of this substance could be destroyed by hydrolysis with 5% hydrochloric acid. A second toxic principle was also present which could be removed by extraction with ethyl alcohol.

Davis, Mehrhof, and McKinney (4) found that tung meal autoclaved at 128°C. and 22 pounds pressure was not safe to use in chicken feeds. Bryan (3) inferred that the toxic principle was a toxalbumin and devised a simple method of detoxifying press cake, the details of which have never been made public. The Louisiana State Experiment Station reported (10) that the toxicity of meal from expellers decreased markedly on storage, but not of meal from solvent extraction. It reported further that meal can be completely detoxified by a combination of heat and alcohol extraction, but the protein of meal detoxified in this way is of little value as a supplement to cereal proteins. The toxic principle which is soluble in alcohol is heat stable under conditions unfavorable to oxidation, but is easily destroyed in the presence of the ferric ion and by saponification with alcoholic potash.

Tung cake guaranteed to contain 4% nitrogen sold for $18.00 per ton for fertilizer in 1952. In 1949 cottonseed and peanut meals sold for about $1.53 per ton percent of protein. If tung cake could be sold for feed on a par with these meals, it would be worth 1.53 x 23.1 or $35.30 per ton. On this basis there is considerable incentive for the detoxification of the meal, as there is a difference of $17.30 per ton to cover costs of transportation, detoxifying, and profits, if the detoxification can be accomplished at a cost well within this amount.

Use in Plastics. Proteins from soybeans and milk have been used for plastics. Unless the proteins of tung kernels have some particularly desirable characteristic which the more abundant oilseed meals like soybeans, etc., do not have, it is doubtful that tung meal could compete with the other sources since they are available in much larger quantities and are in a much purer form than is the meal of tung fruits.

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TABLE I

Composition of Fresh Tung Hulls a/

Component	Fresh hulls			
	Outer hulls	Inner hulls	Shells	Total hulls
Pentosans, %	3.3	18.5	15.0	8.9
Lignin, %	27.0	26.0	51.3	35.3
Cellulose, %	20.7	46.2	23.4	24.3
a-cellulose, %	17.1	31.9	18.7	19.2
Nitrogen, %	0.60	0.52	0.59	0.59
Potash, %	3.17	3.06	1.13	2.45
Phosphoric acid, %	0.32	0.30	0.27	0.30
Ash, %	6.19	4.90	2.69	4.84
Hot water extract, %	38.6	11.7	6.5	24.7
Alcohol extract, %	7.8	3.7	17.1	10.6
Copper, p.p.m.	7	13	28	15
Iron, p.p.m.	69	153	59	74
Manganese, p.p.m.	112	89	71	95

a/ Analyses computed to a moisture-free basis.

TABLE II

Composition of Weathered Tung Hulls[a/]

Component	Weathered two months				Weathered six months			
	Outer hulls	Inner hulls	Shells	Total hulls	Outer hulls	Inner hulls	Shells	Total hulls
Pentosans, %	2.5	19.7	17.1	9.8	2.2	17.5	17.0	9.8
Lignin, %	38.8	27.5	49.0	41.3	54.8	31.8	51.0	50.7
Cellulose, %	22.1	48.0	37.1	30.5	20.2	36.2	29.2	25.6
a-cellulose, %	14.7	32.0	31.3	22.7	13.0	27.0	22.8	18.5
Nitrogen, %	0.64	0.54	0.49	0.57	0.74	0.63	0.48	0.63
Potash, %	2.51	2.37	1.12	1.98	2.16	2.07	0.53	1.51
Phosphoric acid, %	0.34	0.30	0.23	0.30	0.34	0.30	0.21	0.28
Ash, %	5.06	4.01	2.33	3.94	5.27	4.08	1.41	3.61
Hot water extract, %	22.2	9.1	6.4	14.9	9.8	7.7	5.9	8.0
Alcohol extract, %	4.2	3.1	18.6	9.4	2.8	2.3	15.9	7.9
Copper, p.p.m.	-	-	-	-	-	-	-	-
Iron, p.p.m.	-	-	-	-	-	-	-	-
Manganese, p.p.m.	-	-	-	-	-	-	-	-

a/ Analyses computed to a moisture-free basis.

TABLE III

Composition of Tung Press Cake a/

Constituent	Average of 25 Samples	Standard deviation	Range
Oil, %	6.10	1.96	4.3 - 12.1
Crude fiber, %	42.9	3.78	31.8 - 49.9
Pentosans, %	11.3	0.92	9.8 - 13.3
Nitrogen, %	3.97	0.54	2.95 - 4.86
Ash, %	5.35	0.75	4.50 - 8.29
Phosphoric acid, %	1.28	0.17	0.96 - 1.67
Potash, %	2.69	0.27	2.07 - 3.22
Copper b/, p.p.m.	12		
Iron b/, p.p.m.	99		
Manganese b/, p.p.m.	76		

a/ Analyses calculated to a moisture-free basis.
b/ Determined on 1 sample only.

Figure 1. Tung Fruit and Its Components

The fruit (1) consists of four or five seeds (5), each of which is enclosed by a thin inner hull (4), and the whole surrounded by a fibrous outer hull (3) about 1/4 inch thick. Cross sections (2) show the arrangement of the seeds in the fruit. The seeds consist of kernels (7) surrounded by a thin hard shell (6). The kernels constitute about 33% of the dry fruit, the shell 21%, the inner hull 7%, and the outer hull 39%. The dry kernel contains about 65% oil.